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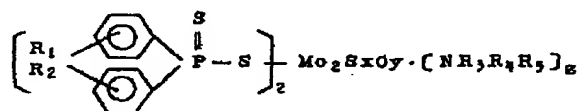
## Specification

### 1. Title of the Invention

Lubricating Oil Compositions and Production of Compounds  
Used Therein

### 2. Claims

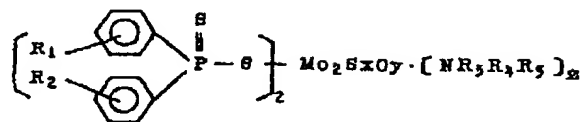
A lubricating composition comprising as an essential component a compound of the general formula:



(wherein  $R_1$  and  $R_2$  may be the same or different, each representing a hydrogen atom, halogen atom or alkyl group of 1-25 carbon atoms;  $R_3$  is an alkyl group of 1-25 carbon atoms, and  $R_4$  and  $R_5$  may be the same or different, each representing a hydrogen atom or alkyl group of 1-25 carbon atoms;  $x$  is a number of an average of 0-2,  $y$  is a number of an average of 2-4, and  $x + y + 1$  is equal to the charge number of molybdenum atom; and  $z$  is a number of an average of more than 0 to 2 or

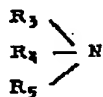
less).

2. A process for producing a molybdenum compound of the general formula:



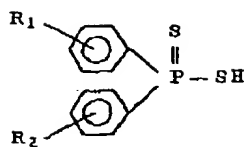
(wherein  $\text{R}_1$  and  $\text{R}_2$  may be the same or different, each representing a hydrogen atom, halogen atom or alkyl group of 1-25 carbon atoms;  $\text{R}_3$  is an alkyl group of 1-25 carbon atoms, and  $\text{R}_4$  and  $\text{R}_5$  may be the same or different, each representing a hydrogen atom or alkyl group of 1-25 carbon atoms;  $x$  is a number of an average of 0-2,  $y$  is a number of an average of 2-4, and  $x + y + 1$  is equal to the charge number of molybdenum atom; and  $z$  is a number of an average of more than 0 to 2 or less)

which comprises reacting a salt or coordination compound or mixture of molybdic acid and an alkylamine of the general formula:



(wherein  $\text{R}_3$  is an alkyl group of 1-25 carbon atoms, and  $\text{R}_4$  and  $\text{R}_5$  each represents a hydrogen atom or alkyl group of 1-25 carbon atoms)

with a diphenylphosphinodithioic acid of the general formula:



(wherein  $R_1$  and  $R_2$  each represents a hydrogen atom, halogen atom or alkyl group of 1-25 carbon atoms, and  $R_1$  and  $R_2$  may be the same or different)

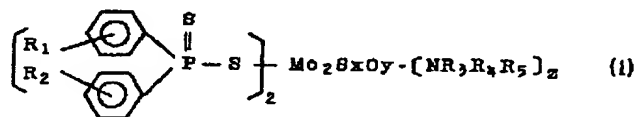
or a reactive derivative thereof.

### 3. Detailed Description of the Invention

The present invention relates to anti-wear and extreme pressure compositions containing a molybdenum compound, particularly a coordination compound of an oxymolybdenum sulfide diphenylphosphinodithioate and an amine or its substituted derivative. The invention also relates to a process for producing a coordination compound of an oxymolybdenum sulfide diphenyl-phosphinodithioate and an amine or its substituted derivatives.

The purpose of the invention is to provide lubricating oil compositions excellent in anti-wear and extreme pressure properties and a novel process for producing them.

The lubricating oil compositions of the invention contain as an essential component a compound of the general formula:



(wherein  $R_1$  and  $R_2$  may be the same or different, each

representing a hydrogen atom, halogen atom or alkyl group of 1-25 carbon atoms;  $R_3$  is an alkyl group of 1-25 carbon atoms, and  $R_4$  and  $R_5$  may be the same or different, each representing a hydrogen atom or alkyl group of 1-25 carbon atoms;  $x$  is a number of an average of 0-2,  $y$  is a number of an average of 2-4, and  $x + y + 1$  is equal to the charge number of molybdenum atom; and  $z$  is a number of an average of more than 0 to 2 or less)

usually in many cases together with a lubricating oil (fats and oils, mineral oil, etc.), grease, and the like.

In the general formula (1), when  $R_1$  and  $R_2$  each is an alkyl group, the carbon number is preferably 1-20, particularly 1-16, but those in which  $R_1$  and  $R_2$  each is hydrogen atom are also preferred.

In the formula, when  $R_3$ ,  $R_4$  and  $R_5$  each represents an alkyl group, the carbon number is preferably 1-20, particularly 8-16, but when  $R_3$  and  $R_4$  each is an alkyl group of 12 or more carbon atoms,  $R_5$  may be a lower alkyl group such as methyl or ethyl.

The molybdenum compound added to the compositions of the invention was confirmed to work as an extreme pressure additive and be able to protect a movable metal surface from wear.

The molybdenum compound used in the compositions of the invention is a complex coordinating with an alkylamine. It is particularly important that when the molybdenum compound free from the alkylamine is a solid material insoluble in

lubricating oil, coordination with an amine converts the solid material into oil to make it soluble in the lubricating oil yielding a preferred form as an additive for the lubricating oil.

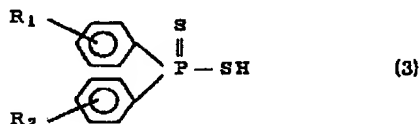
The above-mentioned compounds as additives to the compositions of the invention may be produced according to the following process.

Briefly, the process comprises reacting a salt or coordination compound or mixture of molybdic acid and an alkylamine of the general formula:



(wherein  $R_3$  is an alkyl group of 1-25 carbon atoms, and  $R_4$  and  $R_5$  each represents a hydrogen atom or alkyl group of 1-25 carbon atoms)

with a diphenylphosphinodithioic acid of the general formula:



(wherein  $R_1$  and  $R_2$  each represents a hydrogen atom, halogen atom or alkyl group of 1-25 carbon atoms, and  $R_1$  and  $R_2$  may be the same or different)

or a reactive derivative thereof.

The alkyl amine represented by the general formula (2) used in this process includes, for example, tri-n-hexylamine, tri-n-octylamine, di-n-octyl-iso-octylamine, tri-n-

decylamine, tri-laurylamine, di-lauryl-methylamine, di-lauryl-ethylamine, di-palmityl-methylamine, di-stearyl-methylamine, di-stearylamine, di-palmitylamine, dilaurylamine, stearylamine, palmitylamine, laurylamine, and the like.

Molybdic acid may preferably be provided in a form of an aqueous solution in the following manner. For example, molybdenum trioxide is dissolved in a solution of an alkali metal hydroxide or magnesium oxide or ammonium hydroxide, and the solution is adjusted at pH 0.1 to 4 with addition of an excess amount of a strong mineral acid such as sulfuric acid.

Though molybdic acid mainly contains  $\text{Mo}^{\text{V}}$ , those of more than or less than pentavalent are included, and so the value of  $x$  and  $y$  in the general formula (1) is calculated by subtracting 1 from an average of the charge number of molybdenum.

Using these alkylamines and molybdic acid, first, the alkylamine or sulfate thereof is dissolved in an inert solvent such as low viscosity petroleum hydrocarbon, for example, benzene, toluene, etc. The solution is then mixed with an aqueous molybdic acid solution adjusted at pH 0.1-4 with a strong acid such as sulfuric acid to extract the molybdic acid coordinated with the amine salt or amine sulfate into the organic layer. Thus, molybdic acid may be obtained in a form of salt or coordination compound or mixture. As the

alkylamines, accordingly, an amine sparingly soluble in water or an amine sulfate sparingly soluble in water may preferably be used.

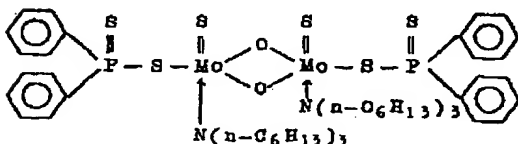
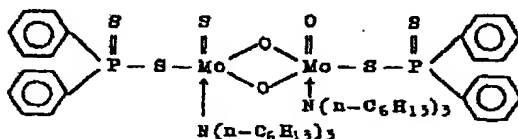
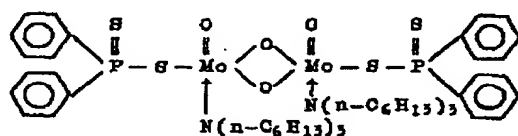
The diphenylphosphinodithioic acid of the general formula (3) or a reactive derivative thereof used in the invention includes phosphinodithioic acids to which is attached a variety of isomeric benzene rings having an alkyl group or groups such as undecyl, dodecyl or tridecyl at the positions 2, 3, 4, etc., for example, raw materials for soaps, such as diphenyldithio-phosphinodithioic acid, di-(p-chlorophenyl)-phosphinodithioic acid, di-(p-methylphenyl)phos-phinodithioic acid, di-p-(ethylphenyl)phosphino-dithioic acid, p-chlorophenyl-p-methylphenylphos-phinodithioic acid, di-(p-octylphenyl)phosphino-dithioic acid, di-(p-dodecylphenyl)phosphinodithioic acid (similarly as alkylbenzenes as raw materials for detergents, phosphinodithioic acid derivatives to which a multi-branched propylene tetramer is attached on the benzene ring, including a variety of isomers), di-(p-undecylphenyl)phosphinodithioic acid, di-(p-dodecylphenyl)phosphinodithioic acid, or di-(p-tri-decylphenyl)phosphinodithioic acid.

The diphenylphosphinodithioic acid or a reactive derivative thereof and the above (thio)molybdic acid amine salt or molybdic acid coordinated with an amine sulfate are added

to a petroleum hydrocarbon solution containing a molybdic acid amine salt or molybdic acid coordinated with amine sulfate at a ratio of 2 moles of diphenylphosphinodithioic acid or its substituted derivative to 1 mole of molybdic acid. The mixture is allowed to react at a temperature of 60-100°C for a period of 1-10 hours to give the aimed compound.

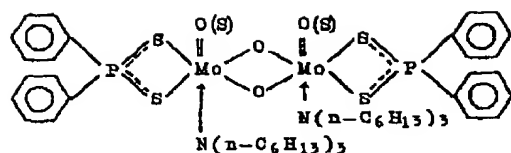
The reaction mixture after cooling is washed with water or a weak alkaline aqueous solution such as sodium carbonate, and the solvent used in the reaction is distilled off to recover the reaction product.

Thus resulting molybdenum-containing compounds can be considered to have the following structural formula, for example, when they consist of 1 mole of molybdic acid, 2 moles of diphenyldithiophosphino-dithioic acid, and 2 moles of tri-n-hexylamine.



and in a certain case,





(in case of  $\text{Mo}^{\text{VI}}$ )

In any cases, it is appropriate to consider that though the amine coordinates to the Mo atom through the unpaired electrons of the amine (1 mole or less for 1 mole of Mo atom), practically the produced compound is not a single substance but a mixture of those compounds.

The above molybdenum-containing compound may be added to lubricating oil or grease generally at a rate of 0.2 to 20wt%, particularly 0.2 to 10wt%. Further, it may contain a lubricating agent mainly consisting of known petroleum such as turbine oil, light oil, SAE90 gear oil, and heavy oil, as well as a known synthetic lubricating agent such as ester, polyether, and silicone. In addition, it is possible to add a usual additive such as thickener (e.g., clay, pigment, alkali metal soap, alkaline earth metal soap or other soap), corrosion inhibitor, anti-oxidant, rust preventives, viscosity improver, pour point depressant, cleaner, extreme pressure agent, anti-wear agent, and the like.

The effects of the invention exist in providing lubricating compositions excellent in anti-wear and extreme pressure properties, and a novel process for producing them.

Example 1

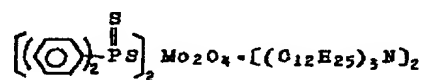
Oxymolybdenum sulfide diphenylphosphinodithioate tri-laurylamine-coordination compound was prepared as follows.

A solution of 48.4 parts of sodium molybdate dihydrate dissolved in 150 parts of water was adjusted at pH 1.5 with conc. sulfuric acid was placed together with 50% benzene solution of 124 parts of trilaurylamine sulfate in a flask equipped with a stirrer, thermometer and refluxing condenser. The mixture was stirred at room temperature for 10 minutes, and then 100 parts of diphenylphosphinodithioic acid was added thereto and allowed to react at 90°C for 5 hours.

The organic layer was separated from the reaction mixture, washed with water and then with 50% bicarbonate aqueous solution, and evaporated to remove benzene to give 316 parts of bluish green oily material.

The analytical data were as follows.

Calcd. for



N (1.5%), Mo (10.6%), S (7.1%)

Found: N (1.3%), Mo (9.9%), S (6.8%)

The infrared absorption spectrum showed the following absorption characteristics (indicated by  $\text{cm}^{-1}$ ).

Strong peaks: 2900, 1110

Medium peaks: 1470, 1040, 1020, 950, 750, 720, 610

Weak peaks: 1380, 850, 580, 330

#### Example 2

Oxymolybdenum sulfide di-(p-chlorophenyl)-phosphinodithioate tri-n-octylamine-coordination compound was prepared as follows.

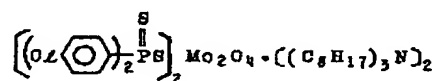
In a flask equipped with a stirrer, thermometer and refluxing condenser was placed 48.4 parts of sodium molybdate dihydrate and 150 parts of water. The mixture was adjusted at pH 0.5 with slow addition of conc. sulfuric acid. There was added 50% benzene solution of 71 parts of tri-n-octylamine, and the mixture was stirred for 10 minutes. Then, 50% benzene solution of 128 parts of di-(p-chlorophenyl)phosphinodithioic acid was added thereto, and the mixture was allowed to stand at 90°C for 5 hours.

The reaction mixture was worked up in the same manner as in Example 1 to give 281 parts of greenish brown oily material.

The analytical data were as follows.

Calcd. for

:



Cl (9.2%), Mo (12.3%), N (8.0%), P (4.0%), S (8.2%)

Found: Cl (8.8%), Mo (11.9%), N (8.1%), P (3.8%), S (8.0%)

#### Example 3

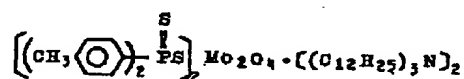
In the same operation and method as in Example 1, the

reaction was conducted at a temperature of 90°C for 4 hours using 111 parts of di-(p-methylphenyl)dithioic acid in place of diphenylphosphinodithioic acid. The reaction mixture was worked up in the same manner as in Example 1 to give 330 parts of the dark brown oily product.

The analytical data were as follows.

Calcd. for

:



N (1.5%), Mo (10.3%), P (3.3%), S (6.9%)

Found: N (1.5%), Mo (9.7%), P (3.2%), S (7.4%)

#### Example 4

The reaction was carried out in the same manner as in Example 1, wherein 91 parts of tri-n-octylamine sulfate was used in place of tri-laurylamine sulfate, and 246 parts of di-(p-tridecylphenyl)phosphinodithioic acid (derived from a linear alkylbenzene of average molecular weight 260 of a raw material for detergent) was used in place of diphenylphosphinodithioic acid. In this reaction, however, a mixture of an aqueous solution of molybdic acid and a benzene solution of trioctylamine sulfate was preliminarily stirred for 10 minutes, and the aqueous layer was recovered from the flask. To this aqueous layer was added the above di-(p-tridecyl-phenyl)phosphinodithioic acid, and the mixture was allowed to react at 90°C for 5 hours and worked up in the same

manner as in Example 1 to give a dark greenish brown oily material.

The analytical data were as follows.

Found: N (1.1%), Mo (8.5%), P (2.8%), S (5.9%)

The infrared absorption spectrum showed nearly the same absorption characteristics as the compound of Example 1.

#### Example 5

In grease containing 9 g of lithium 12-hydroxystearate alone for 100 g of the composition was dispersed or dissolved the molybdenum compound prepared in Example 1 or 2 in an amount of 0.005 mole for 100 g of the composition to give the composition of the invention. In order to demonstrate that the resulting composition containing the molybdenum compound has been improved in anti-wear and extreme pressure properties, the following test was conducted. For comparison, a specimen containing no molybdenum compound of the invention and another specimen containing 0.01 mole/100 g composition of molybdenum disulfide were also tested in the same way.

Such a grease composition was placed on a Timken lubrication-testing machine to conduct a Timken endurance test determining anti-wear properties. A Timken load test determining the extreme pressure properties was also conducted. In the Timken endurance test, 0.5 g of the grease composition was evenly applied on a hard steel ring, which was rotated at 800 rpm. On the other hand, the ring was loaded with a hard

copper block under pressure of 10 pounds for 8 hours to measure the width of wear produced on the block.

The Timken load test was carried out for 10 minutes according to the method as described in ASTM D-2509-68 under variable loading to determine the maximum load under which abnormal wear was produced. That value was recorded as O.K. load. The following table shows the test results.

Sample Name	Time	Wear Width(m/m)	O.K.load (pound)
Compound of Example 1	8	0.8	70
Compound of Example 2	8	0.8	70
MOB <sub>2</sub>	-	-	10
No additive	0	unmeasurable due to seizure	10

#### Example 6

Mineral neutral oil SAE No.90 of which the Saybolt viscosity was 86.8 seconds at 210°F and 936 seconds at 100°F and the viscosity index was 103 was used for the composition. To 100 g of this composition was added 0.002 mole of the molybdenum compound prepared in Example 1, 3 or 4 to produce the composition of the invention. The following tests were conducted in order to demonstrate that the addition of the molybdenum compound could improve the anti-wear and extreme pressure properties. For comparison, a sample (base oil) containing no molybdenum compound was also tested.

The anti-wear properties were confirmed as follows. A ball rotating at 1800 rpm was loaded with 40 kg and made contact with 3 fixed balls, on which the wear width produced by wear

was measured after a lapse of 1 hour to calculate the average value. The extreme pressure properties were confirmed by measuring the average Hertzian pressure and seizure load according to the regulation of the American Federal Standard. In this test, the definite load from low to high was applied for 10 seconds, respectively, and the measurement was made up to seizure to obtain 20 measured values. The average load at the close contact was calculated from the wear width, from which load was calculated the average Hertzian pressure. The following table shows the test results.

Sample Name	Wear Width(m/m)	Seizure load (kg)	Average Hertzian press. (kg)
Compound of Example 1	0.48	206	47
Compound of Example 4	0.43	225	49
Equimolar mixture of Example 3 and Example 4	0.42	225	49
No additive	unmeasurable due to seizure	110	16